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<p>(54) Title: PROCESS FOR APPLYING A LEAD-FREE COATING TO UNTREATED METAL SUBSTRATES VIA ELECTRODEPOSITION</p> <p>(57) Abstract</p> <p>An improved process for applying a lead-free coating by electrodeposition to an untreated ferrous metal substrate is provided. The substrate need not be phosphated prior to treatment. The process includes the following steps: a) contacting the substrate surface with a group IIIB or IVB metal compound in a medium that is essentially free of accelerators needed to form phosphate conversion coating; followed by b) electrocoating the substrate with a substantially lead-free, curable electrodepositable composition; and c) curing the electrodepositable composition. The group IIIB or IVB metal compound is preferably a zirconium compound and is typically in an aqueous medium. The process may further include initial steps of cleaning the substrate with an alkaline cleaner and rinsing with an acidic rinse. Substrates treated by the process of the present invention demonstrate excellent corrosion resistance.</p>		

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**PROCESS FOR APPLYING A LEAD-FREE COATING TO UNTREATED METAL
SUBSTRATES VIA ELECTRODEPOSITION**

BACKGROUND OF THE INVENTION

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The present invention relates to an improved process for applying a lead-free coating via electrodeposition to a metal substrate, including ferrous substrates such as cold rolled steel and electrogalvanized steel, and to the coated
10 substrates produced by this process.

Pretreating metal substrates with a phosphate conversion coating and chrome-containing rinses has long been conventional for promoting corrosion resistance. To maximize corrosion resistance over steel substrates, cationic
15 electrodeposition compositions are conventionally formulated with lead as either a pigment or a soluble lead salt and are applied over pretreated (phosphated and chrome rinsed) substrates. Disadvantages associated with phosphating include the amount of plant space required for processing due to
20 multiple (usually eleven to twenty-five) stages; high capital cost; and generation of waste streams containing heavy metals, requiring expensive treatment and disposal. Additionally, lead and chromium used in the electrodepositable composition can cause environmental concerns. The lead may be present in
25 the effluent from electrodeposition processes and chromium may be present in the effluent from pretreatment processes, and these metals need to be removed and disposed of safely, which again requires expensive waste treatment processes.

Nickel-free phosphate solutions and chrome-free rinsing
30 compositions demonstrating corrosion resistance comparable to the nickel- and chrome-containing forerunners are now being sought. Likewise, lead-free electrodepositable compositions are being developed.

U. S. Patent No. 3,966,502 discloses treatment of
35 phosphated metals with zirconium-containing rinse solutions.

International Patent publication WO 98/07770 discloses lead-free electrodepositable compositions for use over phosphated metals. Neither reference teaches treatment or coating processes for bare metal substrates; i. e., metals that have
5 not been phosphated.

It would be desirable to provide a process for coating metal substrates, particularly bare ferrous metals, using compositions that overcome the environmental drawbacks of the prior art and which demonstrate excellent corrosion
10 resistance.

SUMMARY OF THE INVENTION

In accordance with the present invention, an improved process for applying a lead-free coating by electrodeposition
15 to an untreated metal substrate is provided. By "untreated" is meant a bare metal surface; i. e., one that has not been phosphated. The process comprises the following steps:

a) contacting the substrate surface with a group IIIB or IVB metal compound in a medium, typically an aqueous medium,
20 that is essentially free of accelerators needed to form phosphate conversion coatings; followed by

b) electrocoating the substrate with a substantially lead-free, curable electrodepositable composition; and

c) curing the electrodepositable composition.

25 The process may further include initial steps of cleaning the substrate with an alkaline cleaner and rinsing with an acidic rinse.

DETAILED DESCRIPTION

30 Other than in the operating examples, or where otherwise indicated, all numbers expressing quantities of ingredients or reaction conditions used in the specification and claims are to be understood as modified in all instances by the term "about".

35 The process of the present invention is typically used to treat cold rolled steel substrates, but can be used to treat other metal substrates such as galvanized steel and aluminum,

which are used in the assembly of automobile bodies along with cold rolled steel. Moreover, the bare metal substrate being treated by the process of the present invention may be a cut edge of a substrate that is otherwise treated and/or coated
5 over the rest of its surface.

The substrate to be coated is usually first cleaned to remove grease, dirt, or other extraneous matter. This is done by employing conventional cleaning procedures and materials. These would include mild or strong alkaline cleaners such as
10 are commercially available and conventionally used in metal pretreatment processes. Examples of alkaline cleaners include Chemkleen 163 and Chemkleen 177, both of which are available from PPG Industries, Pretreatment and Specialty Products. Such cleaners are generally followed and/or preceded by a
15 water rinse.

Following the optional cleaning step, the metal surface is contacted with a group IIIB or IVB metal compound which is in a medium that is essentially free of accelerators needed to form phosphate conversion coatings. Such accelerators include
20 hydroxylamine, sodium nitrite, and other accelerators known in the art. It is believed that because no phosphate crystal structures are to be formed on the metal substrate surface, no accelerators are necessary. The medium may also be substantially free of phosphates, particularly phosphates of
25 other metals such as zinc, iron, and other metals typically used in phosphating pretreatment processes.

The group IIIB or IVB metal compound is typically in an aqueous medium, usually in the form of an aqueous solution or dispersion depending on the solubility of the metal compound
30 being used. The aqueous solution or dispersion of the group IIIB or IVB metal compound may be applied to the metal substrate by known application techniques, such as dipping or immersion, which is preferred, spraying, intermittent spraying, dipping followed by spraying or spraying followed by
35 dipping. Typically, the aqueous solution or dispersion is applied to the metal substrate at solution or dispersion temperatures ranging from ambient to 150°F (ambient to 65°C),

and preferably at ambient temperatures. The contact time is generally between 10 seconds and five minutes, preferably 30 seconds to 2 minutes when dipping the metal substrate in the aqueous medium or when the aqueous medium is sprayed onto the metal substrate.

The IIIB or IVB transition metals and rare earth metals referred to herein are those elements included in such groups in the CAS Periodic Table of the Elements as is shown, for example, in the *Handbook of Chemistry and Physics*, 63rd Edition (1983).

Preferred group IIIB and IVB transition metal compounds and rare earth metal compounds are compounds of zirconium, titanium, hafnium, yttrium and cerium and mixtures thereof. Typical zirconium compounds may be selected from hexafluorozirconic acid, alkali metal and ammonium salts thereof, ammonium zirconium carbonate, zirconyl nitrate, zirconium carboxylates and zirconium hydroxy carboxylates such as hydrofluorozirconic acid, zirconium acetate, zirconium oxalate, ammonium zirconium glycolate, ammonium zirconium lactate, ammonium zirconium citrate, and mixtures thereof. Hexafluorozirconic acid is preferred. An example of the titanium compound is fluorotitanic acid and its salts. An example of the hafnium compound is hafnium nitrate. An example of the yttrium compound is yttrium nitrate. An example of the cerium compound is cerous nitrate. The group IIIB or IVB metal compound is present in the medium in an amount of 10 to 5000 ppm metal, preferably 100 to 300 ppm metal. The pH of the aqueous medium usually ranges from 2.0 to about 7.0, preferably about 3.5 to 5.5. The pH of the medium may be adjusted using mineral acids such as hydrofluoric acid, fluoroboric acid, phosphoric acid, and the like, including mixtures thereof; organic acids such as lactic acid, acetic acid, citric acid, or mixtures thereof; and water soluble or water dispersible bases such as sodium hydroxide, ammonium hydroxide, ammonia, or amines such as triethylamine, methylethyl amine, diisopropanolamine, or mixtures thereof.

Additionally, the medium may contain a resinous binder. Suitable resins include reaction products of one or more alkanolamines and an epoxy-functional material containing at least two epoxy groups, such as those disclosed in U. S. 5 5,653,823. Preferably, such resins contain beta hydroxy ester, imide, or sulfide functionality, incorporated by using dimethylolpropionic acid, phthalimide, or mercaptoglycerine as an additional reactant in the preparation of the resin. Alternatively, the reaction product is that of the diglycidyl 10 ether of Bisphenol A (commercially available from Shell Chemical Company as EPON 880), dimethylol propionic acid, and diethanolamine in a 0.6 to 5.0:0.05 to 5.5:1 mole ratio. Other suitable resinous binders include water soluble and water dispersible polyacrylic acids as disclosed in U. S. 15 Patents 3,912,548 and 5,328,525; phenol formaldehyde resins as described in U. S. Patent 5,662,746; water soluble polyamides such as those disclosed in WO 95/33869; copolymers of maleic or acrylic acid with allyl ether as described in Canadian patent application 2,087,352; and water soluble and 20 dispersible resins including epoxy resins, aminoplasts, phenol-formaldehyde resins, tannins, and polyvinyl phenols as discussed in U. S. Patent 5,449,415, incorporated herein by reference.

In this embodiment of the invention, the resinous binder 25 is present in the medium in an amount of 0.005% to 30%, preferably 0.5 to 3%, based on the total weight of the ingredients in the medium, and the group IIIB or IVB metal compound is present in an amount of 10 to 5000, preferably 100 to 1000, ppm metal.

30 The medium may optionally contain other materials such as nonionic surfactants and auxiliaries conventionally used in the art of pretreatment. In an aqueous medium, water dispersible organic solvents, for example, alcohols with up to about 8 carbon atoms such as methanol, isopropanol, and the 35 like, may be present; or glycol ethers such as the monoalkyl ethers of ethylene glycol, diethylene glycol, or propylene glycol, and the like. When present, water dispersible organic

solvents are typically used in amounts up to about ten percent by volume, based on the total volume of aqueous medium.

Other optional materials include surfactants that function as defoamers or substrate wetting agents. Anionic, cationic, amphoteric, or nonionic surfactants may be used. Compatible mixtures of such materials are also suitable. Defoaming surfactants are typically present at levels up to about 1 percent, preferably up to about 0.1 percent by volume, and wetting agents are typically present at levels up to about 2 percent, preferably up to about 0.5 percent by volume, based on the total volume of medium.

The film coverage of the residue of the pretreatment coating composition generally ranges from about 1 to about 1000 milligrams per square meter (mg/m^2), and is preferably about 10 to about 400 mg/m^2 .

The thickness of the pretreatment coating can vary, but is generally less than about 1 micrometer, preferably ranges from about 1 to about 500 nanometers, and more preferably is about 10 to about 300 nanometers.

Other optional steps may be included in the process of the present invention. For example, the metal surface may be rinsed with an aqueous acidic solution after cleaning with the alkaline cleaner and before contact with the group IIIB or IVB metal compound. Examples of rinse solutions include mild or strong acidic cleaners such as the dilute nitric acid solutions commercially available and conventionally used in metal pretreatment processes.

After contact with the group IIIB or IVB metal compound the substrate may be rinsed with water and electrocoated directly; i. e., without a phosphating step as is conventional in the art. Electrocoating may be done immediately or after a drying period at ambient or elevated temperature conditions. The electrocoating step is done with a substantially lead-free, curable, electrodepositable composition and is followed by a curing step.

In the process of electrodeposition, the metal substrate being treated, serving as an electrode, and an electrically

conductive counter electrode are placed in contact with an ionic, electrodepositable composition. Upon passage of an electric current between the electrode and counter electrode while they are in contact with the electrodepositable
5 composition, an adherent film of the electrodepositable composition will deposit in a substantially continuous manner on the metal substrate.

Electrodeposition is usually carried out at a constant voltage in the range of from about 1 volt to several thousand
10 volts, typically between 50 and 500 volts. Current density is usually between about 1.0 ampere and 15 amperes per square foot (10.8 to 161.5 amperes per square meter) and tends to decrease quickly during the electrodeposition process, indicating formation of a continuous self-insulating film.

15 After electrodeposition, the coating is heated to cure the deposited composition. The heating or curing operation is usually carried out at a temperature in the range of from 120 to 250°C, preferably from 120 to 190°C for a period of time ranging from 10 to 60 minutes. The thickness of the resultant
20 film is usually from about 10 to 50 microns.

Preferably in the electrocoating step, the metal substrate being treated serves as a cathode, and the electrodepositable composition is cationic.

In a preferred embodiment of the invention, the
25 substantially lead-free, curable cationic electrodepositable composition contains an amine salt group-containing resin derived from a polyepoxide. The resin is used in combination with a polyisocyanate curing agent that is at least partially capped with a capping agent.

30 In a particularly preferred embodiment, the cationic resin is derived from a polyepoxide, which may be chain extended by reacting together a polyepoxide and a polyhydroxyl group-containing material selected from alcoholic hydroxyl group-containing materials and phenolic hydroxyl group-
35 containing materials to chain extend or build the molecular weight of the polyepoxide. The resin contains cationic salt

groups and active hydrogen groups selected from aliphatic hydroxyl and primary and secondary amino.

A chain extended polyepoxide is typically prepared by reacting together the polyepoxide and polyhydroxyl group-
5 containing material neat or in the presence of an inert organic solvent such as a ketone, including methyl isobutyl ketone and methyl amyl ketone, aromatics such as toluene and xylene, and glycol ethers such as the dimethyl ether of diethylene glycol. The reaction is usually conducted at a
10 temperature of about 80°C to 160°C for about 30 to 180 minutes until an epoxy group-containing resinous reaction product is obtained.

The equivalent ratio of reactants; i. e., epoxy:polyhydroxyl group-containing material is typically from
15 about 1.00:0.75 to 1.00:2.00.

The polyepoxide preferably has at least two 1,2-epoxy groups. In general the epoxide equivalent weight of the polyepoxide will range from 100 to about 2000, typically from about 180 to 500. The epoxy compounds may be saturated or
20 unsaturated, cyclic or acyclic, aliphatic, alicyclic, aromatic or heterocyclic. They may contain substituents such as halogen, hydroxyl, and ether groups.

Examples of polyepoxides are those having a 1,2-epoxy equivalency greater than one and preferably about two; that
25 is, polyepoxides which have on average two epoxide groups per molecule. The preferred polyepoxides are polyglycidyl ethers of cyclic polyols. Particularly preferred are polyglycidyl ethers of polyhydric phenols such as Bisphenol A. These polyepoxides can be produced by etherification of polyhydric
30 phenols with an epihalohydrin or dihalohydrin such as epichlorohydrin or dichlorohydrin in the presence of alkali. Besides polyhydric phenols, other cyclic polyols can be used in preparing the polyglycidyl ethers of cyclic polyols. Examples of other cyclic polyols include alicyclic polyols,
35 particularly cycloaliphatic polyols such as 1,2-cyclohexane diol and 1,2-bis(hydroxymethyl)cyclohexane. The preferred polyepoxides have molecular weights ranging from about 180 to

500, preferably from about 186 to 350. Epoxy group-containing acrylic polymers can also be used, but they are not preferred.

Examples of polyhydroxyl group-containing materials used to chain extend or increase the molecular weight of the polyepoxide (i. e., through hydroxyl-epoxy reaction) include alcoholic hydroxyl group-containing materials and phenolic hydroxyl group-containing materials. Examples of alcoholic hydroxyl group-containing materials are simple polyols such as neopentyl glycol; polyester polyols such as those described in U. S. Patent No. 4,148,772, incorporated herein by reference; polyether polyols such as those described in U. S. Patent No. 4,468,307, incorporated herein by reference; and urethane diols such as those described in U. S. Patent No. 4,931,157, incorporated herein by reference. Examples of phenolic hydroxyl group-containing materials are polyhydric phenols such as Bisphenol A, phloroglucinol, catechol, and resorcinol. Mixtures of alcoholic hydroxyl group-containing materials and phenolic hydroxyl group-containing materials may also be used. Bisphenol A is preferred.

The polyepoxide also contains cationic salt groups. The cationic salt groups are preferably incorporated into the resin by reacting the epoxy group-containing resinous reaction product prepared as described above with a cationic salt group former. By "cationic salt group former" is meant a material which is reactive with epoxy groups and which can be acidified before, during, or after reaction with the epoxy groups to form cationic salt groups. Examples of suitable materials include amines such as primary or secondary amines which can be acidified after reaction with the epoxy groups to form amine salt groups, or tertiary amines which can be acidified prior to reaction with the epoxy groups and which after reaction with the epoxy groups form quaternary ammonium salt groups. Examples of other cationic salt group formers are sulfides which can be mixed with acid prior to reaction with the epoxy groups and form ternary sulfonium salt groups upon subsequent reaction with the epoxy groups.

When amines are used as the cationic salt formers, monoamines are preferred, and hydroxyl-containing amines are particularly preferred. Polyamines may be used but are not recommended because of a tendency to gel the resin.

5 Tertiary and secondary amines are preferred to primary amines because primary amines are polyfunctional with respect to epoxy groups and have a greater tendency to gel the reaction mixture. If polyamines or primary amines are used, they should be used in a substantial stoichiometric excess to
10 the epoxy functionality in the polyepoxide so as to prevent gelation and the excess amine should be removed from the reaction mixture by vacuum stripping or other technique at the end of the reaction. The epoxy may be added to the amine to ensure excess amine.

15 Examples of hydroxyl-containing amines are alkanolamines, dialkanolamines, trialkanolamines, alkyl alkanolamines, and aralkyl alkanolamines containing from 1 to 18 carbon atoms, preferably 1 to 6 carbon atoms in each of the alkanol, alkyl and aryl groups. Specific examples include ethanolamine, N-
20 methylethanolamine, diethanolamine, N-phenylethanolamine, N,N-dimethylethanolamine, N-methyldiethanolamine, triethanolamine and N-(2-hydroxyethyl)-piperazine.

Amines such as mono, di, and trialkylamines and mixed aryl-alkyl amines which do not contain hydroxyl groups or
25 amines substituted with groups other than hydroxyl which do not negatively affect the reaction between the amine and the epoxy may also be used. Specific examples include ethylamine, methylethylamine, triethylamine, N-benzyl dimethylamine, dicocoamine and N,N-dimethylcyclohexylamine.

30 Mixtures of the above mentioned amines may also be used.

The reaction of a primary and/or secondary amine with the polyepoxide takes place upon mixing of the amine and polyepoxide. The amine may be added to the polyepoxide or vice versa. The reaction can be conducted neat or in the
35 presence of a suitable solvent such as methyl isobutyl ketone, xylene, or 1-methoxy-2-propanol. The reaction is generally exothermic and cooling may be desired. However, heating to a

moderate temperature of about 50 to 150°C may be done to hasten the reaction.

The reaction product of the primary and/or secondary amine and the polyepoxide is made cationic and water dispersible by at least partial neutralization with an acid. Suitable acids include organic and inorganic acids such as formic acid, acetic acid, lactic acid, phosphoric acid and sulfamic acid. Sulfamic acid is preferred. The extent of neutralization varies with the particular reaction product involved. However, sufficient acid should be used to disperse the electrodepositable composition in water. Typically, the amount of acid used provides at least 20 percent of all of the total neutralization. Excess acid may also be used beyond the amount required for 100 percent total neutralization.

In the reaction of a tertiary amine with a polyepoxide, the tertiary amine can be prereacted with the neutralizing acid to form the amine salt and then the amine salt reacted with the polyepoxide to form a quaternary salt group-containing resin. The reaction is conducted by mixing the amine salt with the polyepoxide in water. Typically the water is present in an amount ranging from about 1.75 to about 20 percent by weight based on total reaction mixture solids.

In forming the quaternary ammonium salt group-containing resin, the reaction temperature can be varied from the lowest temperature at which the reaction will proceed, generally room temperature or slightly thereabove, to a maximum temperature of about 100°C (at atmospheric pressure). At higher pressures, higher reaction temperatures may be used. Preferably the reaction temperature is in the range of about 60 to 100°C. Solvents such as a sterically hindered ester, ether, or sterically hindered ketone may be used, but their use is not necessary.

In addition to the primary, secondary, and tertiary amines disclosed above, a portion of the amine that is reacted with the polyepoxide can be a ketimine of a polyamine, such as is described in U. S. Patent No. 4,104,147, column 6, line 23 to column 7, line 23, incorporated herein by reference. The

ketimine groups decompose upon dispersing the amine-epoxy resin reaction product in water.

In addition to resins containing amine salts and quaternary ammonium salt groups, cationic resins containing
5 ternary sulfonium groups may be used in forming the cationic polyepoxide. Examples of these resins and their method of preparation are described in U. S. Patent Nos. 3,793,278 to DeBona and 3,959,106 to Bosso et al., incorporated herein by reference.

10 The extent of cationic salt group formation should be such that when the resin is mixed with an aqueous medium and the other ingredients, a stable dispersion of the electrodepositable composition will form. By "stable dispersion" is meant one that does not settle or is easily
15 redispersible if some settling occurs. Moreover, the dispersion should be of sufficient cationic character that the dispersed particles will migrate toward and electrodeposit on a cathode when an electrical potential is set up between an anode and a cathode immersed in the aqueous dispersion.

20 Generally, the cationic resin is non-gelled and contains from about 0.1 to 3.0, preferably from about 0.1 to 0.7 millequivalents of cationic salt group per gram of resin solids. The number average molecular weight of the cationic polyepoxide preferably ranges from about 2,000 to about
25 15,000, more preferably from about 5,000 to about 10,000. By "non-gelled" is meant that the resin is substantially free from crosslinking, and prior to cationic salt group formation, the resin has a measurable intrinsic viscosity when dissolved in a suitable solvent. In contrast, a gelled resin, having an
30 essentially infinite molecular weight, would have an intrinsic viscosity too high to measure.

The active hydrogens associated with the cationic polyepoxide include any active hydrogens which are reactive with isocyanates within the temperature range of about 93 to
35 204 °C, preferably about 121 to 177°C. Typically, the active hydrogens are selected from the group consisting of hydroxyl and primary and secondary amino, including mixed groups such

as hydroxyl and primary amino. Preferably, the polyepoxide will have an active hydrogen content of about 1.7 to 10 millequivalents, more preferably about 2.0 to 5 millequivalents of active hydrogen per gram of resin solids.

5 Beta-hydroxy ester groups may be incorporated into the polyepoxide by ring opening 1,2-epoxide groups of the polyepoxide with a material which contains at least one carboxylic acid group. The carboxylic acid functional material may be a monobasic acid such as dimethylolpropionic
10 acid, malic acid, and 12-hydroxystearic acid; a polybasic acid such as a simple dibasic acid or the half ester reaction products of a polyol and the anhydride of a diacid, or a combination thereof. If a monobasic acid is used, it preferably has hydroxyl functionality associated with it.
15 Suitable polybasic acids include succinic acid, adipic acid, citric acid, and trimellitic acid. If a polybasic acid is used, care must be taken to prevent gelation of the reaction mixture by limiting the amount of polybasic acid and/or by additionally reacting a monobasic acid. Suitable half ester
20 reaction products include, for example, the reaction product of trimethylolpropane and succinic anhydride at a 1:1 equivalent ratio. Suitable hydroxyl group-containing carboxylic acids include dimethylolpropionic acid, malic acid, and 12-hydroxystearic acid. Dimethylolpropionic acid is
25 preferred.

Phenolic hydroxyl groups may be incorporated into the polyepoxide by using a stoichiometric excess of the polyhydric phenol during initial chain extension of the polyepoxide. Although a stoichiometric excess of phenolic hydroxyl groups
30 to epoxy is used, there still remains unreacted epoxy groups in the resulting resinous reaction product for subsequent reaction with the cationic salt group former. It is believed that a portion of polyhydric phenol remains unreacted.

When the polyepoxide contains both phenolic hydroxyl
35 groups and beta-hydroxy ester groups, the phenolic hydroxyl groups may be incorporated simultaneously with the beta-hydroxy ester groups, or sequentially before or after.

Preferably, however, the phenolic hydroxyl groups are incorporated into the polyepoxide after incorporation of the beta-hydroxy ester groups by reacting a stoichiometric excess of polyhydric phenol with the resulting polyepoxide. Once
5 again, despite the stoichiometric excess of phenolic hydroxyl groups to epoxy being used, unreacted epoxy groups remain in the resulting resinous reaction product for subsequent reaction with the cationic salt group former.

In this particularly preferred embodiment, the
10 polyisocyanate curing agent is a fully capped polyisocyanate with substantially no free isocyanate groups. The polyisocyanate can be an aliphatic or an aromatic polyisocyanate or a mixture of the two. Diisocyanates are preferred, although higher polyisocyanates can be used in
15 place of or in combination with diisocyanates.

Examples of suitable aliphatic diisocyanates are straight chain aliphatic diisocyanates such as 1,4-tetramethylene diisocyanate and 1,6-hexamethylene diisocyanate. Also, cycloaliphatic diisocyanates can be employed. Examples
20 include isophorone diisocyanate and 4,4'-methylene-bis-(cyclohexyl isocyanate). Examples of suitable aromatic diisocyanates are p-phenylene diisocyanate, diphenylmethane-4,4'-diisocyanate and 2,4- or 2,6-toluene diisocyanate. Examples of suitable higher polyisocyanates are
25 triphenylmethane-4,4',4"-triisocyanate, 1,2,4-benzene triisocyanate and polymethylene polyphenyl isocyanate.

Isocyanate prepolymers, for example, reaction products of polyisocyanates with polyols such as neopentyl glycol and trimethylol propane or with polymeric polyols such as
30 polycaprolactone diols and triols (NCO/OH equivalent ratio greater than one) can also be used. A mixture of diphenylmethane-4,4'-diisocyanate and polymethylene polyphenyl isocyanate is preferred.

Any suitable aliphatic, cycloaliphatic, or aromatic alkyl
35 monoalcohol or phenolic compound may be used as a capping agent for the polyisocyanate including, for example, lower aliphatic alcohols such as methanol, ethanol, and n-butanol;

cycloaliphatic alcohols such as cyclohexanol; aromatic-alkyl alcohols such as phenyl carbinol and methylphenyl carbinol; and phenolic compounds such as phenol itself and substituted phenols wherein the substituents do not affect coating operations, such as cresol and nitrophenol. Glycol ethers may also be used as capping agents. Suitable glycol ethers include ethylene glycol butyl ether, diethylene glycol butyl ether, ethylene glycol methyl ether and propylene glycol methyl ether. Diethylene glycol butyl ether is preferred among the glycol ethers.

Other suitable capping agents include oximes such as methyl ethyl ketoxime, acetone oxime and cyclohexanone oxime, lactams such as epsilon-caprolactam, and amines such as dibutyl amine.

Beta-hydroxy ester groups may be incorporated into the polyisocyanate by reacting the isocyanate groups of the polyisocyanate with the hydroxyl group of a hydroxyl group-containing carboxylic acid such as dimethylolpropionic acid, malic acid, and 12-hydroxystearic acid. Dimethylolpropionic acid is preferred. The acid group on the hydroxyl group-containing carboxylic acid is reacted (either before or after reaction of the isocyanate group with the hydroxyl group) with an epoxy functional material such as a monoepoxide or polyepoxide, ring opening a 1,2-epoxide group on the epoxy functional material to form the beta-hydroxy ester group. Examples of monoepoxides which may be used include ethylene oxide, propylene oxide, 1,2-butylene oxide, 1,2-pentene oxide, styrene oxide, and glycidol. Other examples of monoepoxides include glycidyl esters of monobasic acids such as glycidyl acrylate, glycidyl methacrylate, glycidyl acetate, glycidyl butyrate; linseed glycidyl ester and glycidyl ethers of alcohols and phenols such as butyl glycidyl ether and phenylglycidyl ether.

Examples of polyepoxides which may be used to form the beta-hydroxy ester groups in the polyisocyanate are those having a 1,2-epoxy equivalency greater than one and preferably about two; that is, polyepoxides which have on average two

epoxide groups per molecule. The preferred polyepoxides are polyglycidyl ethers of cyclic polyols. Particularly preferred are polyglycidyl ethers of polyhydric phenols such as Bisphenol A.

5 Phenolic hydroxyl groups may be incorporated into the polyisocyanate by capping the isocyanate groups with phenolic materials having an aliphatic and a phenolic hydroxyl group such as 2-hydroxybenzyl alcohol. The isocyanate group will react preferentially with the aliphatic hydroxyl group. It is
10 also possible to incorporate phenolic hydroxyl groups into the polyisocyanate by capping the isocyanate groups with a hydroxyl functional polyepoxide such as a polyglycidyl ether of a cyclic polyol or polyhydric phenol, which is further reacted with a stoichiometric excess of a polyhydric phenol.

15 These electrodepositable compositions may further include additional ingredients having beta-hydroxy ester and/or phenolic hydroxyl groups, as well as customary auxiliaries typically used in electrodepositable compositions. Such electrodepositable compositions are described in WO 98/07770.

20 Untreated metal substrates coated by the process of the present invention demonstrate excellent corrosion resistance as determined by salt spray corrosion resistance testing. The excellent corrosion resistance is unexpected since the phosphating step has been eliminated, and results are
25 comparable to corrosion resistance obtainable with lead-containing electrodepositable compositions.

The invention will be further described by reference to the following examples. Unless otherwise indicated, all parts are by weight.

30

EXAMPLES

In accordance with the present invention, the following examples show the preparation of various zirconium-containing aqueous pretreatments, their application to bare ferrous and
35 galvanized substrates, and comparative corrosion testing results.

Preparation of Panels for Corrosion Testing

Bare, or untreated cold rolled steel and electrogalvanized substrates used in preparing test panels were purchased from ACT Laboratories, Inc., Hillsdale, MI.

5 The panels treated in the examples that follow have all been pretreated in the following process sequence unless otherwise noted in the example. The term "ambient temperature" in the subsequent examples describes conditions at about 20-30°C. All pretreatment compositions were adjusted to the pH indicated in
10 the tables below with 10% ammonium hydroxide or 1% sulfamic acid, and measured at ambient temperatures using a Digital Ionalyzer Model SA720, commercially available from Orion Research.

15 General panel preparation sequence:

Stage #1 "CHEMKLEEN 163", an alkaline cleaner available from PPG Industries, Inc. sprayed @ 2% by volume at 0-65°C for 1-2 minutes.

20 Stage #2 Tap water immersion rinse 15-30 seconds, ambient temperature.

Stage #3 Immersion in non-phosphate containing aqueous pretreatment solution, 60 seconds, ambient temperature.

25 Stage #4 Deionized water immersion rinse, 15-30 seconds, ambient temperature.

Optionally, an immersion in a 2% by volume nitric acid solution for 5-15 seconds followed by a tap water rinse can be done following stage #2 and before stage #3. Following stage
30 #4, an optional drying with warm air can be done before electrodeposition of the leaded or lead-free composition. The leaded composition was ED 5650 available from PPG Industries, Inc. The unleaded composition was similar to ED 5650 but with the lead removed.

Panels prepared by the above procedure produce very thin films on the order of 7-10 nm as determined by depth profiling X-ray photoelectron spectroscopy and profilometry.

Panels were electrocoated with the lead containing or
5 lead-free electrodepositable coatings. After curing of the electrodepositable paint, panels were scribed with either a large X for testing in salt spray (per ASTM B117) or warm salt water immersion (5% NaCl solution in deionized water maintained at 55°C), or a straight vertical line for cyclic
10 corrosion testing (per General Motors 9540P, 'Cycle B'). After testing was complete (lengths for each test protocol detailed in the tables below), panels were grit blasted to remove corrosion products and delaminated paint. Panels were evaluated by measuring the total creepback of the paint from
15 each side of the scribe at two points where paint loss was at the minimum and maximum. Data is reported in the tables as a range in millimeters.

The compositions of the various zirconium-containing pretreatments that were tested are listed in Table I. All
20 compositions were prepared by adding the appropriate amount of material listed in the table to a portion of deionized water with stirring. Enough deionized water was then added to bulk the solution to one liter. The pH of the pretreatment solutions was then adjusted to the value in the table by
25 dropwise addition of 10% ammonium hydroxide if the initial pH was < 4.5, and 1% sulfamic acid if the initial pH was > 4.5.

TABLE I
Composition of Pretreatment Examples 2-9

	Example #, Level in ppm							
Component	<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>	<u>6</u>	<u>7</u>	<u>8</u>	<u>9</u>
Fluorozirconic Acid ¹	398	398						398
Reaction product of EPON 880/DMPA/DEA ²		1000						
Ammonium Zr Carbonate ³			2947	2947				
Zirconyl Nitrate ⁴					444	444		
Ammonium Zr Citrate ⁴							675	
Chemseal 77 ⁵								1000
pH	4.5	4.5	8.6	5.5	5.5	4.4	5.8	4.6

¹available from Riedel de Haën as a 45% aqueous solution

²reacted in a 10/3.5/2.5 mole ratio and dispersed to 70% total neutralization in sulfamic acid

³available from Magnesium Elektron, Inc. as a 20% solution

⁴available from Aldrich Chemical Company

⁵conventional non-chrome post-rinse for phosphated substrates available from PPG Pretreatment and Specialty Chemicals, compositions disclosed in US Patent 5,653,823

Note that panels of Example 1 underwent only stages 1 and 2 of the above procedure; i. e., no immersion in non-phosphate containing aqueous pretreatment solution took place.

Corrosion Results from Salt Spray Testing

The corrosion resistance produced by pretreatment compositions listed in Table I was measured according to ASTM B117, entitled "Standard Test Method of Salt Spray (Fog) Testing." Panels prepared as in Example 1 were painted with either a lead-containing (comparative) available from PPG Industries, Inc. as ED 5650 or a lead-free electrodepositable composition similar to the lead-containing electrocoat but without the lead to determine the strength of each variation as a new pretreatment for lead-free electrodepositable paint relative to lead-containing compositions.

TABLE II
Salt Spray Test (ASTM B117) 600 hrs

Bath Example #	ED Type	Scribe Creep (mm)	
		Bare CRS	Bare EG
1 (Alkaline clean only)	Leaded	5-8	2-15
	Lead-free	12-17	7-17
2	Leaded	2-4	3-13
	Lead-free	2-3	1-10
3	Leaded	2-3	4-12
	Lead-free	4-5	1-15
4	Leaded	8-10	
	Lead-free	14-17	
5	Leaded	7-10	
	Lead-free	14-16	
6	Leaded	7-9	
	Lead-free	13-15	
7	Leaded	6-8	
	Lead-free	12-16	
8	Leaded	7-9	
	Lead-free	15-17	
9	Leaded	10-13	
	Lead-free	18-20	

The data in Table II illustrate that the corrosion performance on cold rolled steel of the lead-free electrocoat paint is as good as the lead-containing paint when pretreated with the composition detailed in Example #2. Furthermore, the data indicates that when using the composition in Example #2 on electrogalvanized steel, the performance with lead-free electrocoat exceeds the performance with the leaded version.

Corrosion Results from Warm Salt Water Immersion

Bare cold rolled steel and electrogalvanized panels were treated with solutions from Table I via the procedure stages listed above and tested for corrosion resistance using the warm salt water immersion test, which is an immersion in a 5%

NaCl solution in deionized water maintained at 55°C. Panels were coated as described above. Results are summarized in Table III below.

5

TABLE III
Warm Salt Water Immersion (20 days)

<u>Bath Example #</u>	<u>ED Type</u>	<u>Scribe Creep (mm)</u>	
		<u>Bare CRS</u>	<u>Bare EG</u>
1 (Alkaline clean only)	Leaded	24-26	5-16
	Lead-free	TD ⁶	8-14
2	Leaded	12-19	3-9
	Lead-free	18-20	5-9
3	Leaded	15-18	4-7
	Lead-free	17-18	3-12
4	Leaded	14-19	
	Lead-free	>35	
5	Leaded	14-15	
	Lead-free	>35	
6	Leaded	15-18	
	Lead-free	>35	
7	Leaded	17-19	
	Lead-free	>35	
8	Leaded	13-16	
	Lead-free	30-32	
9	Leaded	16-19	
	Lead-free	TD	

⁶Total Delamination of paint from substrate

The data reflects the greater severity of this test as reflected in the higher scribe creep ranges. However, a noticeable improvement relative to the clean only control, is again observed on both substrates using the pretreatment described in Example #2.

10

Corrosion Results from Cycle B Testing

Bare cold rolled steel and electrogalvanized panels were treated with solutions from Table I and tested for corrosion performance using the Cycle B cyclic corrosion test as per
 5 General Motors Test Method 9540P. Panels prepared from bath compositions in Table I were prepared and painted as in the examples above. Results are summarized in Table IV below.

TABLE IV

10 Cycle B Corrosion Results on Cold Rolled Steel (30 cycles)

<u>Bath Example #</u>	<u>ED Type</u>	<u>Scribe creep</u>
1 (Alkaline clean only)	Leaded	5-6
	Lead-free	TD
2	Leaded	4-5
	Lead-free	3-4
3	Leaded	4-5
	Lead-free	4-5
4	Leaded	4-5
	Lead-free	6-7
5	Leaded	4-5
	Lead-free	7-9
6	Leaded	4-5
	Lead-free	7-9
7	Leaded	5-6
	Lead-free	6-7
8	Leaded	4-5
	Lead-free	7-9
9	Leaded	4-5
	Lead-free	7-9

⁶Total Delamination of paint from substrate

From the data in Tables II-IV, it is apparent that corrosion performance of a lead-free electrodepositable
 15 coating can be dramatically improved to equal the performance of a lead-containing electrocoat on non-phosphated cold rolled steel and electrogalvanized steel by pretreatment with the

preferred composition described in Example 2 of Table I. This is particular important in using a lead-free electrodepositable coating for painting automobile frames. These frames have hidden or recessed inner parts, frequently
5 made of cold rolled steel which are often poorly phosphated and therefore have traditionally not met corrosion requirements with lead-free coatings.

WE CLAIM:

1. A process for applying a lead-free coating by electrodeposition to an untreated ferrous metal substrate
5 comprising the following steps:
 - a) contacting the substrate surface with a group IIIB or IVB metal compound in a medium that is essentially free of accelerators needed to form phosphate conversion coatings; followed by
 - 10 b) electrocoating the substrate which serves as an electrode in an electrical circuit comprising said electrode and a counter electrode immersed in an aqueous, substantially lead-free curable electrodepositable composition containing an ionic water dispersible resin; and
 - 15 c) heating the electrodeposited film to cure the film.
2. The process of claim 1 further comprising the step of cleaning the metal surface with an alkaline cleaner before contact with the group IIIB or IVB metal compound.
20
3. The process of claim 2 further comprising the step of rinsing the metal surface with an aqueous acidic solution after cleaning with the alkaline cleaner and before contact with the group IIIB or IVB metal compound.
25
4. The process of claim 1 wherein the Group IIIB or IVB metal compound is present in an aqueous medium.
5. The process of claim 4 wherein the substrate is
30 contacted with the Group IIIB or IVB metal compound in the aqueous medium at a temperature of about ambient to 150 °F (ambient to 65°C).
6. The process of claim 4 wherein the substrate is
35 contacted with the Group IIIB or IVB metal compound by immersion.

7. The process of claim 1 wherein the Group IIIB or IVB metal compound is a zirconium compound.

8. The process of claim 7 wherein the zirconium
5 compound is hexafluorozirconic acid.

9. The process of claim 1 wherein the ionic water dispersible resin is a cationic resin.

10 10. The process of claim 9 wherein the cationic water dispersible resin contains amine salt groups and is derived from a polyepoxide.

11. The process of claim 10 wherein the
15 electrodepositable composition further comprises a polyisocyanate curing agent that is at least partially capped with a capping agent.

12. The process of claim 7 wherein the zirconium
20 compound is present in the aqueous medium in an amount of 10 to 5000 ppm Zr.

13. The process of claim 1 wherein the metal substrate is cold rolled steel.
25

14. The process of claim 1 wherein the metal substrate is zinc coated steel.

15. A substrate coated in accordance with the process of
30 claim 1.

INTERNATIONAL SEARCH REPORT

International Application No

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A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C25D13/20

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C25D C23C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 457 790 A (LINDERT ANDREAS ET AL) 3 July 1984 (1984-07-03) column 1, paragraph 1 column 3, paragraph 4 column 6, line 1 - line 10 column 6, line 23 - line 27 column 6, line 50,51 examples 5,6,8 claims 1,12,13	1,2,4-7, 13-15
A	EP 0 281 176 A (METALLGESELLSCHAFT AG) 7 September 1988 (1988-09-07) page 3, line 2 - line 8 examples claims 1,4-6	1-4,7,9, 15



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

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INTERNATIONAL SEARCH REPORT

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PCT/US 00/12672

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 664 348 A (BETZ EUROP INC) 26 July 1995 (1995-07-26) page 3, paragraphs 2,3 table 1 examples claims 1,4	1,2,4,6, 7,13-15
A	WO 96 19595 A (HENKEL CORP ;IINO YASUO (JP); SHIMIZU AKIO (JP); IKEDA TOSHIHIRO () 27 June 1996 (1996-06-27) page 3, paragraph 2 page 10, line 13 - line 16 page 11, line 8 - line 14 page 16, line 6 - line 11	1,3-5,7, 12,15
A	US 5 662 746 A (AFFINITO JOHN C) 2 September 1997 (1997-09-02) cited in the application column 2, line 43 - line 51 column 4, line 34,35,43,44 column 5, line 1 - line 3 column 5, line 40 - line 52 claims	1,2,4-8, 12,13,15
A	EP 0 492 713 A (METALLGESELLSCHAFT AG) 1 July 1992 (1992-07-01) page 2, line 36-51 example 3 claims 1-5,9	1,4-8, 12-15
A	US 5 851 371 A (STEINBRECHER LESTER E ET AL) 22 December 1998 (1998-12-22) abstract column 7, line 58,59 claims 1,2,10,11,15	1,7-9, 14,15
A	WO 98 10024 A (PPG INDUSTRIES INC) 12 March 1998 (1998-03-12) claims 1,2,4,6,25,26	9-11

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 00/12672

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 4457790 A	03-07-1984	AU 575563 B	04-08-1988
		AU 2779684 A	15-11-1984
		BR 8402194 A	18-12-1984
		CA 1214036 A	18-11-1986
		JP 2034606 C	28-03-1996
		JP 7042423 B	10-05-1995
		JP 59207972 A	26-11-1984
		KR 9106787 B	02-09-1991
		MX 164875 B	29-09-1992
		NZ 208079 A	30-09-1987
		PH 21626 A	11-12-1987
		ZA 8403491 A	24-12-1984
EP 0281176 A	07-09-1988	DE 3705633 A	01-09-1988
		BR 8800681 A	04-10-1988
		DE 3865045 A	31-10-1991
		ES 2025763 T	01-04-1992
EP 0664348 A	26-07-1995	US 5328525 A	12-07-1994
		AT 158029 T	15-09-1997
		AU 5223793 A	14-07-1994
		CA 2110456 A	06-07-1994
		DE 69405530 D	16-10-1997
		DE 69405530 T	26-02-1998
		ES 2105357 T	16-10-1997
		AU 669231 B	30-05-1996
WO 9619595 A	27-06-1996	JP 8176841 A	09-07-1996
		AU 4469796 A	10-07-1996
		BR 9510243 A	04-11-1997
		CA 2208459 A	27-06-1996
		CN 1124303 A	12-06-1996
		EP 0799326 A	08-10-1997
		KR 179687 B	18-02-1999
		TR 960620 A	21-07-1996
US 5662746 A	02-09-1997	ZA 9510615 A	03-07-1996
		AT 196323 T	15-09-2000
		AU 703739 B	01-04-1999
		AU 1886297 A	10-09-1997
		BR 9707620 A	27-07-1999
		CN 1212027 A	24-03-1999
		EP 0902844 A	24-03-1999
		WO 9731135 A	28-08-1997
		HU 9900783 A	28-07-1999
		JP 2000506216 T	23-05-2000
		PL 328655 A	15-02-1999
EP 0492713 A	01-07-1992	DE 4041091 A	25-06-1992
		BR 9105374 A	25-08-1992
		CA 2057825 A	22-06-1992
		CS 9103866 A	15-07-1992
		HU 59728 A	29-06-1992
		JP 4276087 A	01-10-1992
		MX 9102653 A	01-06-1992
		PL 292868 A	24-08-1992
		PT 99880 A	31-12-1992

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 00/12672

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 5851371 A	22-12-1998	BR 9607325 A CA 2213824 A EP 0815295 A WO 9627034 A	30-12-1997 06-09-1996 07-01-1998 06-09-1996
WO 9810024 A	12-03-1998	US 5908912 A AU 715805 B AU 4172797 A BR 9711704 A EP 0927232 A	01-06-1999 10-02-2000 26-03-1998 24-08-1999 07-07-1999